CLAIMS

1.   A method of forming an ion of formula (I):
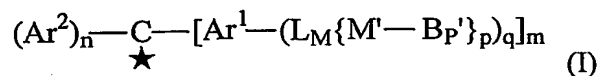
$$(Ar^2)_n - \overset{\bigstar}{C} - [Ar^1 - (L_M\{M' - B_P'\}_p)_q]_m \qquad (I)$$

comprising the steps of:

(i)   reacting a compound of the formula (IIa):

$$(Ar^2)_n - \underset{X}{\overset{|}{C}} - [Ar^1 - (L_M\{M\}_p)_q]_m \qquad (IIa);$$

with a biopolymer, B_P, having at least one group capable of reacting with M to form a covalent linkage, to provide a biopolymer derivative of the formula (IIIa):

$$(Ar^2)_n - \underset{X}{\overset{|}{C}} - [Ar^1 - (L_M\{M' - B_P'\}_p)_q]_m \qquad (IIIa); \text{ and}$$
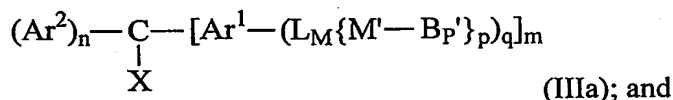
(ii)   cleaving the C—X bond between X and the α-carbon atom of the derivative of formula (IIIa) to form the ion of formula (I);

where:

$C\bigstar$ is a carbon atom bearing a single positive charge or a single negative charge;

X is a group capable of being cleaved from the α-carbon atom to form an ion of formula (I);

M is independently a group capable of reacting with B_P to form the covalent linkage;

B_P' is independently the biopolymer residue of B_P produced on formation of the covalent linkage;

M' is independently the residue of M produced on formation of the covalent linkage;

Ar^1 is independently an aromatic group or an aromatic group substituted with one or more A;

Ar^2 is independently an aromatic group or an aromatic group substituted with one or more A;

optionally wherein (a) two or three of the groups Ar^1 and Ar^2 are linked together by one or more L^5, where L^5 is independently a single bond or a linker atom or group; and/or (b) two or three of the groups Ar^1 and Ar^2 together form an aromatic group or an aromatic group substituted with one or more A;

A is independently a substituent;

L_M is independently a single bond or a linker atom or group;

n = 0, 1 or 2 and m = 1, 2, or 3, provided the sum of n+m = 3;

p independently = 1 or more; and

q independently = 1 or more.

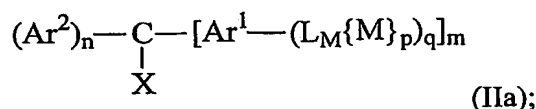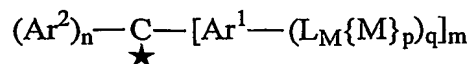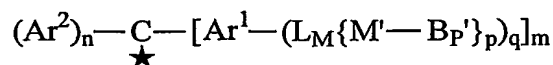2. A method of forming an ion of formula (I), comprising the steps of:

    (i)   reacting a compound of the formula (IIb):

$$(Ar^2)_n - \underset{\bigstar}{C} - [Ar^1 - (L_M\{M\}_p)_q]_m$$

$$X\bigstar \qquad \text{(IIb);}$$

with a biopolymer, B_P, having at least one group capable of reacting with M to form a covalent linkage, to provide a biopolymer derivative of the formula (IIIb):

$$(Ar^2)_n - \underset{\bigstar}{C} - [Ar^1 - (L_M\{M' - B_P'\}_p)_q]_m$$

$$X\bigstar \qquad \text{(IIIb); and}$$

dissociating $X\bigstar$ from the derivative of formula (IIIb), to form the ion of formula (I);

where:

    $X\bigstar$ is a counter-ion to $C\bigstar$;

    and $C\bigstar$, M, B_P', M', Ar^1, Ar^2, L_M, n, m, p and q are as defined in claim 1.

3. A biopolymer derivative of the formula (IIIa).

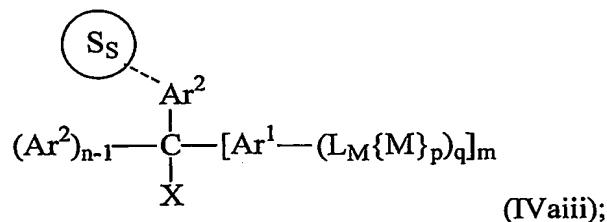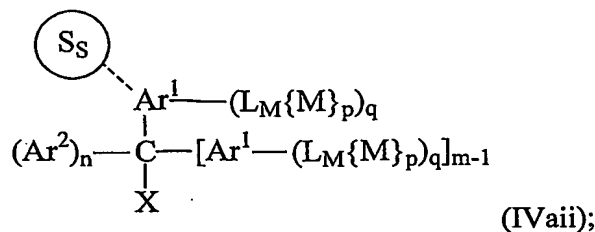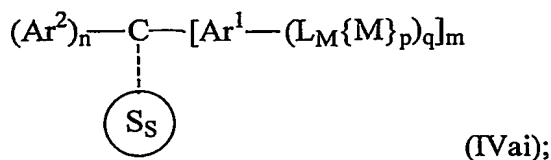4. A biopolymer derivative of the formula (IIIb).

5. An ion of formula (I).

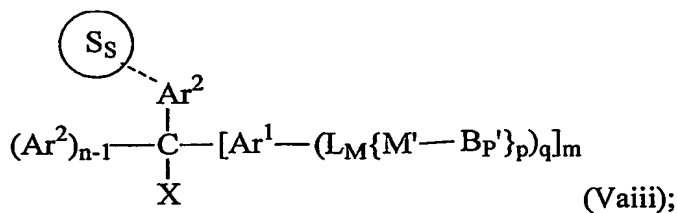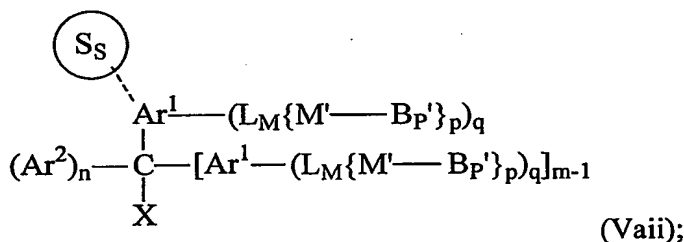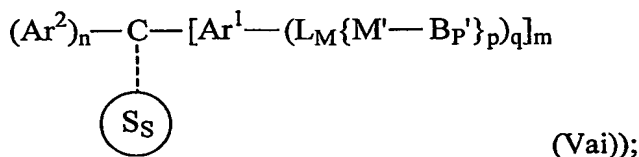6. A compound of the formula (IIa).

7. A compound of the formula (IIb).

8. A method of forming an ion of formula (I) comprising the steps of:

    (i)   reacting a solid support of formula (IVai), (IVaii), or (IVaiii):

$$(Ar^2)_n\text{—}C\text{—}[Ar^1\text{—}(L_M\{M\}_p)_q]_m$$

$$\underset{\displaystyle S_S}{|}$$

(IVai);

$$\overset{\displaystyle S_S}{}$$
$$\overset{.}{Ar^1}\text{—}(L_M\{M\}_p)_q$$
$$(Ar^2)_n\text{—}\underset{X}{\overset{|}{C}}\text{—}[Ar^1\text{—}(L_M\{M\}_p)_q]_{m\text{-}1}$$

(IVaii);

$$\overset{\displaystyle S_S}{}$$
$$\overset{.}{Ar^2}$$
$$(Ar^2)_{n\text{-}1}\text{—}\underset{X}{\overset{|}{C}}\text{—}[Ar^1\text{—}(L_M\{M\}_p)_q]_m$$

(IVaiii);

with a biopolymer, B_P, having at least one group capable of reacting with M to form a covalent
5 linkage, to provide a modified solid support of the formula (Vai), (Vaii), or (Vaiii), respectively:

$$(Ar^2)_n\text{—}C\text{—}[Ar^1\text{—}(L_M\{M'\text{—}B_P'\}_p)_q]_m$$

$$\underset{\displaystyle S_S}{|}$$

(Vai));

$$\overset{\displaystyle S_S}{}$$
$$\overset{.}{Ar^1}\text{—}(L_M\{M'\text{——}B_P'\}_p)_q$$
$$(Ar^2)_n\text{—}\underset{X}{\overset{|}{C}}\text{—}[Ar^1\text{—}(L_M\{M'\text{—}B_P'\}_p)_q]_{m\text{-}1}$$

(Vaii);

$$\overset{\displaystyle S_S}{}$$
$$\overset{.}{Ar^2}$$
$$(Ar^2)_{n\text{-}1}\text{—}\underset{X}{\overset{|}{C}}\text{—}[Ar^1\text{—}(L_M\{M'\text{—}B_P'\}_p)_q]_m$$

(Vaiii);

and either:

10   (iia)   for modified solid supports of formula (Vai) cleaving the C-S_S bond between
the α-carbon atom of the modified solid support of formula (Vai) and the solid support S_S to form the
ion of formula (I);

(iib)   for modified solid supports of formula (Vaii), either simultaneously or sequentially, cleaving the C-X bond between X and the α-carbon atom and cleaving the SS- - -Ar1 bond between the solid support and the Ar1 group to form the ion of formula (I); or

(iic)   for modified solid supports of formula (Vaiii), either simultaneously or sequentially, cleaving the C-X bond between X and the α-carbon atom and cleaving the SS- - -Ar2 bond between the solid support and the Ar2 group to form the ion of formula (I);

where:

X, Ar^1, Ar^2, $B_{P'}$, L_M, M, M', n, m, p and q are as defined in claim 1;
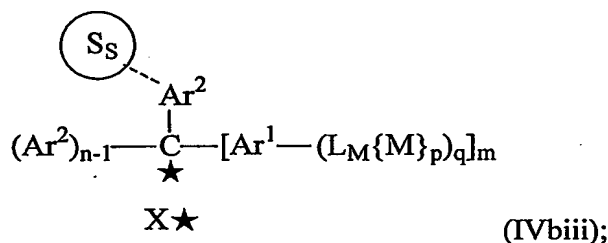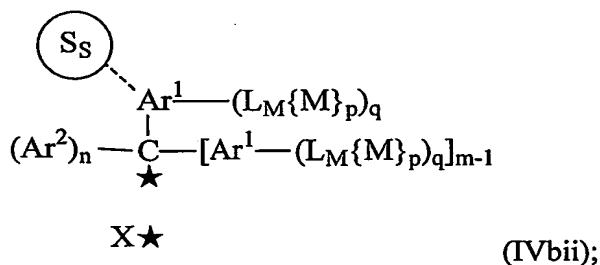
S_S is a solid support;

C- - -S_S comprises a cleavable bond between C and S_S;

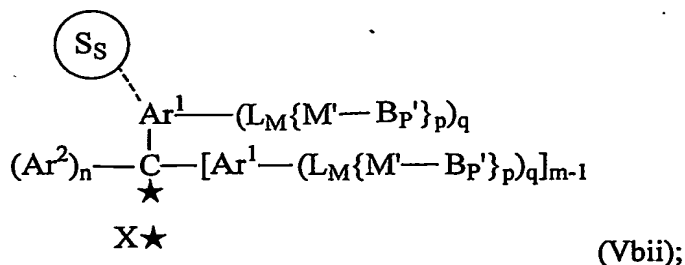S_S- - -Ar^1 comprises a cleavable bond between Ar^1 and S_S; and

S_S- - -Ar^2 comprises a cleavable bond between Ar^2 and S_S.

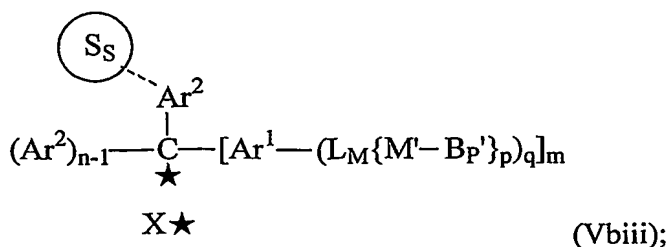9.   A method of forming an ion of formula (I) comprising the steps of:

(i)   reacting a solid support of formula (IVbii) or (IVbiii):

$$(Ar^2)_n - \overset{\displaystyle \overset{\textstyle S_S}{\underset{|}{}}\!\!Ar^1\!\!-\!\!(L_M\{M\}_p)_q}{\underset{\bigstar}{C}}\!\!-\![Ar^1\!\!-\!\!(L_M\{M\}_p)_q]_{m-1}$$

X★   (IVbii);

$$(Ar^2)_{n-1} - \overset{\displaystyle \overset{\textstyle S_S}{\underset{|}{Ar^2}}}{\underset{\bigstar}{C}}\!\!-\![Ar^1\!\!-\!\!(L_M\{M\}_p)_q]_m$$

X★   (IVbiii);

with a biopolymer, B_P, having at least one group capable of reacting with M to form a covalent linkage, to provide a modified solid support of the formula (Vbii) or (Vbiii), respectively:

$$(Ar^2)_n - \overset{\displaystyle \overset{\textstyle S_S}{\underset{|}{}}\!\!Ar^1\!\!-\!\!(L_M\{M'\!\!-\!\!B_{P'}\}_p)_q}{\underset{\bigstar}{C}}\!\!-\![Ar^1\!\!-\!\!(L_M\{M'\!\!-\!\!B_{P'}\}_p)_q]_{m-1}$$

X★   (Vbii);

$$\underset{\displaystyle \overset{\displaystyle \overset{\textstyle \widehat{S_S}}{\vdots}}{\underset{\displaystyle \underset{\displaystyle X\bigstar}{\overset{\displaystyle |}{\underset{\displaystyle \bigstar}{C}}}}{Ar^2}}}{(Ar^2)_{n-1}-\overset{|}{C}-[Ar^1-(L_M\{M'-B_P{}'\}_p)_q]_m}$$
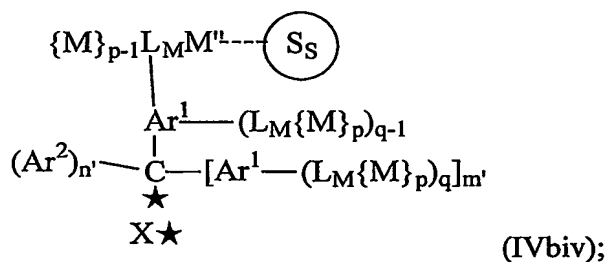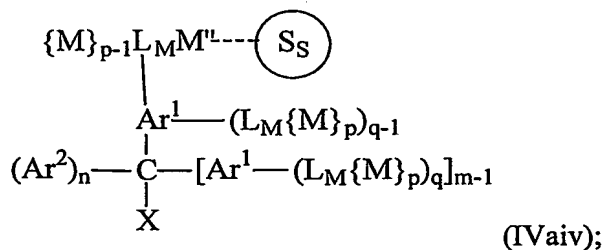
(Vbiii);

and either:

       (iia)   for modified solid supports of formula (Vbii), either simultaneously or sequentially, dissociating $X\bigstar$ from the derivative of formula (Vbii) and cleaving the $S_S\text{- - -}Ar^1$ bond between the solid support and the Ar^1 group to form an ion of formula (I); or

       (iib)   for modified solid supports of formula (Vbiii), either simultaneously or sequentially, dissociating $X\bigstar$ from the derivative of formula (Vbiii) and cleaving the $S_S\text{- - -}Ar^2$ bond between the solid support and the Ar^2 group to form an ion of formula (I);
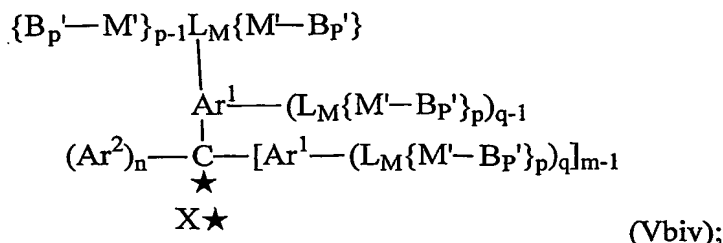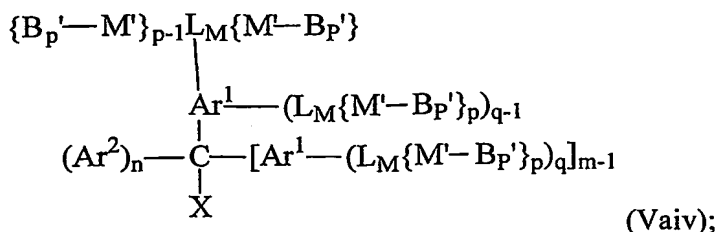
where: $X\bigstar$, Ar^1, Ar^2, $B_P{}'$, L_M, M, M', n, m, p, q, S_S, $C\text{- - -}S_S$, $S_S\text{- - -}Ar^1$ and $S_S\text{- - -}Ar^2$ are as defined in claim 8.

10. A method of forming an ion of formula (I) comprising the steps of:

    (i)   reacting a solid support of formula (IVaiv) or (IVbiv):

$$\underset{\displaystyle \underset{\displaystyle X}{\overset{\displaystyle |}{C}}}{(Ar^2)_n-\overset{\displaystyle \overset{\textstyle \{M\}_{p-1}L_MM'^{L}\text{---}\widehat{S_S}}{\underset{\displaystyle Ar^1\!-\!(L_M\{M\}_p)_{q-1}}{|}}}{\overset{|}{C}}-[Ar^1-(L_M\{M\}_p)_q]_{m-1}}$$

(IVaiv);

$$\underset{\displaystyle \underset{\displaystyle X\bigstar}{\overset{\displaystyle |}{\underset{\bigstar}{C}}}}{(Ar^2)_{n'}-\overset{\displaystyle \overset{\textstyle \{M\}_{p-1}L_MM'^{L}\text{---}\widehat{S_S}}{\underset{\displaystyle Ar^1\!-\!(L_M\{M\}_p)_{q-1}}{|}}}{\overset{|}{C}}-[Ar^1-(L_M\{M\}_p)_q]_{m'}}$$

(IVbiv);

with a biopolymer, B_P, having at least one group capable of reacting with M to form a covalent linkage, to provide a modified solid support of the formula (Vaiv) or (Vbiv), respectively:

$$\{B_p{'}—M'\}_{p\text{-}1}L_M\{M'—B_{P}{'}\}$$
$$\mid$$
$$Ar^1—(L_M\{M'—B_P{'}\}_p)_{q\text{-}1}$$
$$(Ar^2)_n—\overset{\mid}{\underset{\mid}{C}}—[Ar^1—(L_M\{M'—B_P{'}\}_p)_q]_{m\text{-}1}$$
$$X$$

(Vaiv);

$$\{B_p{'}—M'\}_{p\text{-}1}L_M\{M'—B_P{'}\}$$
$$\mid$$
$$Ar^1—(L_M\{M'—B_P{'}\}_p)_{q\text{-}1}$$
$$(Ar^2)_n—\overset{\mid}{\underset{\bigstar}{C}}—[Ar^1—(L_M\{M'—B_P{'}\}_p)_q]_{m\text{-}1}$$
$$X\bigstar$$

(Vbiv);

and either:

(iia)   for modified solid supports of formula (Vaiv), cleaving the C-X bond
between X and the α-carbon atom to form the ion of formula (I); or

(iib)   for modified solid supports of formula (Vbiv), dissociating $X\bigstar$ from the
derivative of formula (Vbiv) to form the ion of formula (I);

where:

X, $X\bigstar$, Ar^1, Ar^2, $B_P{'}$, L_M, M, M', p, q, n, m, and S_S are as defined in claims 8 and 9;

M''---S_S comprises a bond between M'' and S_S; and

M'' is the same as M except that S_S is bound to a portion of M which does not form part of
M'.

11. A solid support of the formula (IVai), (IVaii), (IVaiii), (IVaiv), (IVbii), (IVbiii) or (IVbiv).

12. A modified solid support of the formula (Vai), (Vaii), (Vaiii), (Vaiv), (Vbii), (Vbiii) or
(Vbiv).

13. A method of any of claims 8-10 or a product of claim 11 or 12 wherein the biopolymer is a
synthetic biopolymer.

14. A method or product of claim 13 wherein the synthetic biopolymer is an oligonucleotide, a
peptide or a carbohydrate.

15. A method for analysing a biopolymer, B_P, comprising the steps of:

(i)   reacting the biopolymer B_P with a compound of formula (IIa) or (IIb) or a solid support of formula (IVai), (IVaii), (IVaiii), (IVaiv), (IVbii), (IVbiii) or (IVbiv);

(ii)   providing an ion of formula (I); and

(iii)   analysing the ion of formula (I) by mass spectrometry.

16. In a method for analysing a biopolymer, B_P, the improvement consisting of: (i) reacting a biopolymer, B_P with a compound of formula (IIa) or (IIb) or a solid support of formula (IVai), (IVaii), (IVaiii), (IVaiv), (IVbii), (IVbiii) or (IVbiv); (ii) providing an ion of formula (I); and (iii) analysing the ion by mass spectrometry.

17. A method of claim 15 or claim 16 wherein the analysis by mass spectrometry is carried out in a spectrometer which is suitable for MALDI-TOF spectrometry.

18. A method of any of claims 1, 2, 8-10 or 13-17 or a product of any of claims 3-7, 11 or 12, wherein $C\star$ bears a single positive charge, such that the ions of formulae (I), (IIb) and (IIIb) have the structures:

Formula (I)	$(Ar^2)_n{-}\underset{\oplus}{C}{-}[Ar^1{-}(L_M{-}\{M'{-}B_{P'}\}_p)_q]_m$
Formula (IIb)	$(Ar^2)_n{-}\underset{\oplus}{C}{-}[Ar^1{-}(L_M{-}\{M\}_p)_q]_m$ $X\ominus$
Formula (IIIb)	$(Ar^2)_n{-}\underset{\oplus}{C}{-}[Ar^1{-}(L_M{-}\{M'{-}B_{P'}\}_p)_q]_m$ $X\ominus$

19. A method of any of claims 1, 2, 8-10 or 13-18 or a product of any of claims 3-7, 11, 12 or 18 wherein $n = 2$ and $m = 1$.
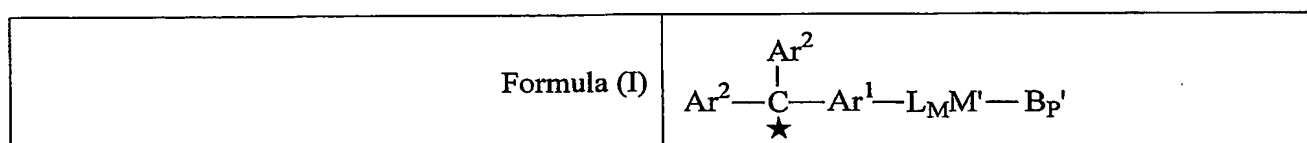
20. A method of any of claims 1, 2, 8-10 or 13-19 or a product of any of claims 3-7, 11, 12, 18 or 19 wherein $p = 1$, 2 or 3.

21. A method of any of claims 1, 2, 8-10 or 13-20 or a product of any of claims 3-7, 11, 12 or 18-20 wherein $p = 1$.

22. A method of any of claims 1, 2, 8-10 or 13-21 or a product of any of claims 3-7, 11, 12 or 18-21 wherein q = 1, 2 or 3.

23. A method of any of claims 1, 2, 8-10 or 13-22 or a product of any of claims 3-7, 11, 12 or 18-22 wherein q = 1.

24. A method of any of claims 1, 2, 8-10 or 13-23 or a product of any of claims 3-7, 11, 12 or 18-23 wherein n = 2, m = 1, p = 1 and q = 1, such that the ion of formula (I) has the structure:
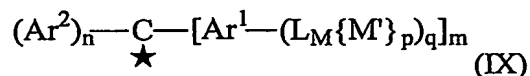
Formula (I)	$$Ar^2 - \overset{\overset{\textstyle Ar^2}{\textstyle |}}{\underset{\textstyle \bigstar}{C}} - Ar^1 - L_M M' - B_P'$$

25. A method of any of claims 1, 2, 8-10 or 13-24 or a product of any of claims 3-7, 11, 12 or 18-24 wherein the biopolymer is a polymer found in biological samples.

26. A method or product of claim 25 wherein the biopolymer is a polypeptide, polysaccharide, or polynucleotide.

27. A method or product of claim 26 wherein the biopolymer is a polypeptide.

28. A method or product of any of claims 25-27 wherein the biopolymer does not readily form a molecular ion on illumination of laser light at 340 nm.

29. A method of any of claims 1, 2, 8-10 or 13-28 or a product of any of claims 3-7, 11, 12 or 18-28 wherein the ratio $m(B_P') / m(IX)$ is more than 2, where $m(IX)$ is the mass of the fragment (IX)

$$(Ar^2)_n - \underset{\bigstar}{C} - [Ar^1 - (L_M\{M'\}_p)_q]_m \quad (IX)$$

of the cation of formula (I) and $m(B_P')$ is the mass of the biopolymer residue B_P'.

30. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein M is: $-NR_2$; $-SR$; $-OR$; $-B(R)Y$; $-BY_2$; $-C(R)_2Y$; $-C(R)Y_2$; $-CY_3$; $-C(=Z)Y$;

-Z-C(=Z)Y; -C(=Z)R; -C(R)(OH)OR; -C(R)(OR)$_2$; -S(=O)Y; -Z-S(=O)Y; -Z-S(=O)$_2$Y; -S(=O)$_2$Y; -S(=O)$_3$Y; -Z-S(=O)$_3$Y; -P(=Z)(ZR)Y; -P(=Z)Y$_2$; -Z-P(=Z)(ZR)Y; -Z-P(=Z)Y$_2$; -P(=Z)(R)Y; -Z-P(=Z)(R)Y; or -N=C(=Z), where Y is independently a leaving group, Z is independently O, S or N(R) and R is independently H, C$_{1-8}$hydrocarbyl or C$_{1-8}$hydrocarbyl substituted with one or more A.

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31. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein M is: -N(R)-; -S-; -O-; -B(Y)-; -C(R)(Y)-; -CY$_2$-; -C(=O)-; -C(OH)(OR)-; or -C(OR)$_2$-, where Y is independently a leaving group and R is independently H, C$_{1-8}$hydrocarbyl or C$_{1-8}$hydrocarbyl substituted with one or more A.

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32. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein M is: $\overset{|}{\underset{}{-\!\!-C(Y)\!\!-\!\!-}}$, where Y is a leaving group.

33. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 15   18-29 wherein the covalent linkage is selected from those produced through the reaction of one the
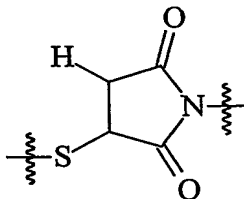
following groups: -CO-NH-; biotin-(strept)avidin;   ; or -NH-CS-NH-.

34. A method of any of claims 1, 2, 8-10 or 13-33 or a product of any of claims 3-7, 11, 12 or 18-33 wherein L$_M$ is O or S.

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35. A method of any of claims 1, 2, 8-10 or 13-33 or a product of any of claims 3-7, 11, 12 or 18-33 wherein L$_M$ is -E^M-, -(D^M)$_t$-, -(E^M-D^M)$_t$-, -(D^M-E^M)$_t$-, -E^M-(D^M-E^M)$_t$- or -D^M-(E^M-D^M)$_t$- (in the orientation Ar^1-(L$_M${M}$_p$)$_q$ or Ar^1-(L$_M${M'}$_p$)$_q$, as appropriate),

where:

25   a sufficient number of linking covalent bonds, in addition to the covalent bonds at the chain termini shown, are provided on groups E^M and D^M for linking the p instances of M (or M') groups;

D^M is independently C$_{1-8}$hydrocarbylene or C$_{1-8}$hydrocarbylene substituted with one or more A;

E^M (in the orientation Ar^1-(L$_M${M}$_p$)$_q$ or Ar^1-(L$_M${M'}$_p$)$_q$, as appropriate) is independently -Z^M-, -C(=Z^M)-, -Z^{M}C(=Z^M)-, -C(=Z^M)Z^M-, -Z^{M}C(=Z^M)Z^M-, -S(=O)-, -Z^{M}S(=O)-, -S(=O)Z^M-,

$-Z^M S(=O)Z^M-$, $-S(=O)_2-$, $-Z^M S(=O)_2-$, $-S(=O)_2 Z^M-$, $-Z^M S(=O)_2 Z^M-$, where Z^M is independently O, S or $N(R^M)$ and where R^M is independently H, C_{1-8}hydrocarbyl (*e.g.* C_{1-8}alkyl) or C_{1-8}hydrocarbyl substituted with one or more A; and
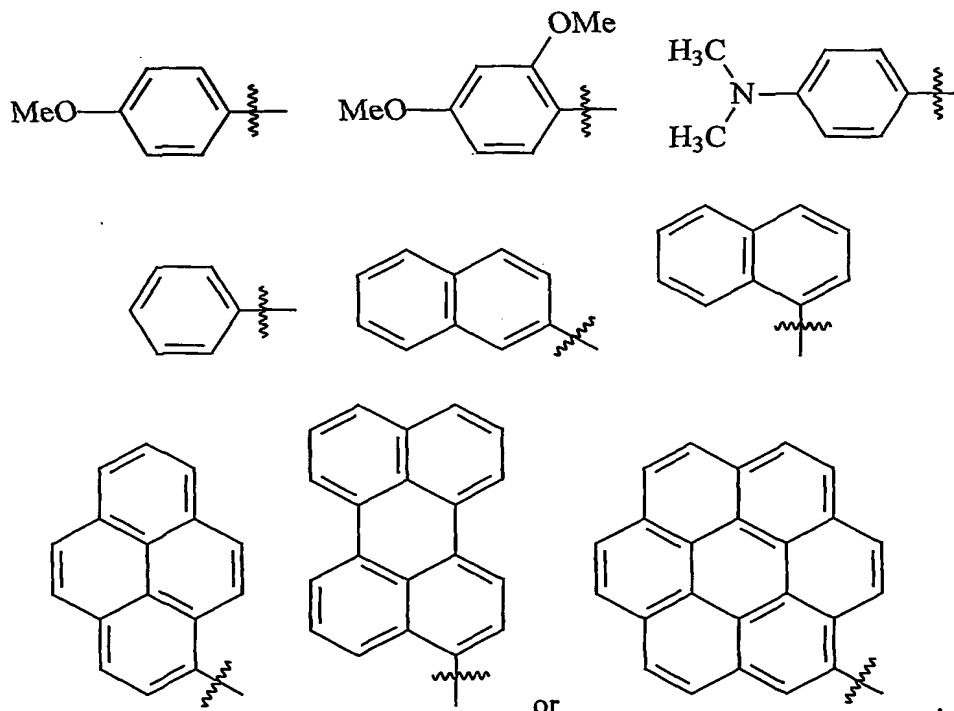
t = 1 or more.

36. A method of any of claims 1, 8, 10 or 13-35 or a product of any of claims 3, 6, 11, 12 or 18-35 wherein the group X is halogen, hydroxy, C_{1-8}hydrocarbyloxy, C_{1-8}hydrocarbyloxy substituted with one or more A, C_{1-8}heterohydrocarbyloxy, C_{1-8}heterohydrocarbyloxy substituted with one or more A, mesyl, tosyl, pentafluorophenyl, -O-succinimidyl -S-succinimidyl, or phenyloxy substituted with one or more A.

37. A method of any of claims 1, 2, 8-10 or 13-36 or a product of any of claims 3-7, 11, 12 or 18-36 wherein Ar^2 is independently cyclopropyl, cyclopropyl substituted with one or more A, aryl, aryl substituted with one or more A, heteroaryl, or heteroaryl substituted with one or more A.

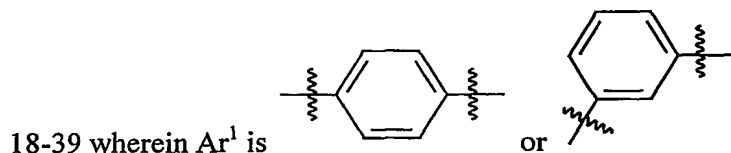38. A method of any of claims 1, 2, 8-10 or 13-37 or a product of any of claims 3-7, 11, 12 or 18-37 wherein Ar^2 is

or

39. A method of any of claims 1, 2, 8-10 or 13-38 or a product of any of claims 3-7, 11, 12 or 18-38 wherein Ar^1 is independently cyclopropylene, cyclopropylene substituted with one or more A, arylene, arylene substituted with one or more A, heteroarylene, or heteroarylene substituted with one or more A.

40. A method of any of claims 1, 2, 8-10 or 13-39 or a product of any of claims 3-7, 11, 12 or 18-39 wherein Ar^1 is

41. A method of any of claims 1, 2, 8-10 or 13-40 or a product of any of claims 3-7, 11, 12 or 18-40 wherein L^5 is O or S.

42. A method of any of claims 1, 2, 8-10 or 13-40 or a product of any of claims 3-7, 11, 12 or 18-40 wherein L^5 is $-E^5-$, $-(D^5)_{t'}-$, $-(E^5-D^5)_{t'}-$, $-(D^5-E^5)_{t'}-$, $-E^5-(D^5-E^5)_{t'}-$ or $-D^5-(E^5-D^5)_{t'}-$,

where:

D^5 is independently C_{1-8}hydrocarbylene or C_{1-8}hydrocarbylene substituted with one or more A;

E^5 is independently $-Z^5-$, $-C(=Z^5)-$, $-Z^5C(=Z^5)-$, $-C(=Z^5)Z^5-$, $-Z^5C(=Z^5)Z^5-$, $-S(=O)-$, $-Z^5S(=O)-$, $-S(=O)Z^5-$, $-Z^5S(=O)Z^5-$, $-S(=O)_2-$, $-Z^5S(=O)_2-$, $-S(=O)_2Z^5-$, $-Z^5S(=O)_2Z^5-$, where Z^5 is independently O, S or $N(R^5)$ and where R^5 is independently H, C_{1-8}hydrocarbyl or C_{1-8}hydrocarbyl substituted with one or more A; and

$t' = 1$ or more.